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Roger Meads, Darryl Spencer and Mario J. Molina

Department of Earth, Atmospheric and Planetary Sciences
and Department of Chemistry

Massachusetts Institute of Technology

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to

TRW Space and Technology Group

One Space Park Drive

Redondo Beach, CA 90278

Attn. Dr. John J. Lamb

Introduction

The emissions from solid rocket motors (SRMs) include hydrogen chloride vapor (HCl) and other inorganic chlorine compounds, as well as aluminum oxide particles. The effects of these emissions on stratospheric ozone have been investigated by Prather et al. [1], Pyle [2], and others. Recent satellite observations show no measurable localized depletion of ozone following a Space Shuttle launch [3]; nevertheless, it is possible for the effects to be quite pronounced in the immediate neighborhood of the rocket plume.

The stratospheric effects of SRM emissions on a global scale might also be of importance. If the altitude of injection is taken into account, the consequences for ozone depletion of chlorine released by SRMs are expected to be practically the same -on an atom per atom basis- as those of chlorine released by the decomposition of CFCs. The reason is that the various inorganic forms of chlorine interconvert to each other on a time scale which is short compared to the residence time of these species in the stratosphere, which is measured in years. A separate effect on stratospheric ozone from SRM emissions is that resulting from the surface chemistry promoted by alumina particles, which could lead to enhanced ozone depletion through catalytic chlorine activation; such an effect is potentially more important than that resulting from the direct chlorine injection. Surface reactions leading to chlorine activation are well documented for stratospheric aerosols at high latitudes, i.e. low temperatures; such heterogeneous reactions play a key role in polar ozone depletion (see e.g., our recent reviews of the stratospheric ozone problem [4,5]). At low latitudes these aerosols consist predominantly of rather concentrated sulfuric acid solutions (> 50 % weight), which are inefficient for chlorine activation because of the very low solubility of HCl in such solutions. On the other hand, alumina particles can in principle promote

chlorine activation catalytically even at low latitudes. In order to assess this possibility, we have carried out laboratory investigations on the chlorine activation efficiency of alumina surfaces; the results are presented in this report.

Cofer and Pellett [6] carried out investigations of the interaction of HCl and H₂O on various types of aluminum oxide surfaces, showing that chemisorption as well as physical adsorption takes place. However, their experiments were not carried out at low temperatures, and more importantly, the H₂O and HCl partial pressures employed were orders of magnitude above those applicable to the stratosphere. Furthermore, little if anything can be inferred from such experiments in terms of the efficiency for chlorine activation in the stratosphere by the surfaces in question.

Reactivity of ClONO₂ + HCl On α -Alumina Surfaces

We have carried out measurements of the reaction probability of ClONO₂ + HCl on α -Alumina surfaces under typical stratospheric conditions of temperature and reactant partial pressures. The experiments were performed in a low pressure - fast flow reactor, operated at steady state, fitted with a movable injector, and coupled to a quadrupole mass spectrometer. This technique is similar to that used previously by our group to measure the reaction probabilities of processes such as ClONO₂ + HCl and HOCl + HCl on ice, NAT and SAT [7,8,9]. The experimental procedure consisted of measuring the reactant ClONO₂ decay and product Cl₂ appearance at steady state in the presence of excess HCl vapor as a function of injector position, and from these we determined the respective pseudo first order rate coefficients. Experiments were conducted in dry Helium buffer gas or Helium humidified with $3-5 \times 10^{-4}$ torr of water at total pressures near 1 torr; there were no significant differences in the reaction rates with water vapor added. The partial pressures of ClONO₂ and HCl were in the range

of 10^{-7} to 10^{-6} torr, which correspond to typical lower stratospheric values. The measured first order rate coefficients, determined by a non-linear least squares fitting routine, were corrected for the effects of radial diffusion [10].

The α -alumina samples employed in our experiments were obtained from Aldrich Chemical Company; they consisted of < 3 mm diameter sintered pieces (with irregular shapes). Although the surface area of these alumina particles was not accurately known, it could be estimated by geometric considerations assuming a non-porous surface. On the other hand, since the detailed flow dynamics -and hence, the surface collision frequency- is difficult to model accurately for the system containing the alumina particles, the reaction probability was determined by comparison to that measured on glass pieces of comparable dimensions. The alumina or glass particles were placed in a Teflon boat, and the walls of the glass flow-tube reactor were covered with a Teflon sleeve which we determined to have a reaction probability at least two orders of magnitude smaller than that of glass. The reaction probability on a glass surface was measured directly in separate experiments using a cylindrical glass tube, for which the flow dynamics is well understood.

Typical measured reactant decays and product buildups are shown in figure 1 to 3; the injector position has been converted to time, taking into account the gas flow velocity. Calculated reaction probabilities are shown in table 1. The reaction probabilities exhibited no measurable temperature dependence over the range -20 to -75 °C.

Control experiments were carried out to measure the reaction probabilities on ice and on 60 wt. % H_2SO_4 surfaces to confirm that we were able to measure the much higher reaction probability on ice -greater than 0.1- and the essentially non-reactivity

on 60 wt. % H_2SO_4 . The results we obtained in these experiments were in good agreement with accepted values. Our measurements yield a reaction probability of $\text{ClONO}_2 + \text{HCl}$ on α -alumina surfaces of 0.01 - 0.02.

Seeding Experiments

Besides chlorine activation, the alumina particles emitted by SRMs have the potential to function as nucleation centers for the formation of polar stratospheric clouds. The more prevalent type I cloud particles are believed to consist of nitric acid trihydrate (NAT). We investigated in the laboratory the ability of alumina particles to nucleate NAT from supercooled nitric acid solutions (3:1 $\text{H}_2\text{O}:\text{HNO}_3$). We found the alumina not to be a good seed for the nucleation of NAT. The control experiment consisted of using NAT crystals as seeds; as expected, these did induce the rapid nucleation of the entire supercooled solution.

Stratospheric Implications

The measured reaction probability of $\text{ClONO}_2 + \text{HCl}$ on α -alumina is an order of magnitude less than that on ice and water-rich NAT surfaces. The role of surfaces such as alumina in the activation of chlorine at polar latitudes is expected to be small and their effect limited, even if the reaction probability were to be above 0.1, given their small abundance relative to polar stratospheric clouds. However, at mid-latitudes, characterized by higher temperatures where ice and NAT do not form, they could have a more significant role in chlorine activation and subsequent ozone depletion. Our results indicate that other related particles such as those of meteoritic origin may also play a role in the depletion of ozone at mid-latitudes.

The background aerosol particles prevalent at low latitudes consist of liquid sulfuric acid solutions with concentrations in the range from about 50 to 70% by weight H_2SO_4 . Chlorine activation on these liquid aerosols occurs extremely inefficiently as a consequence of the very small solubility of HCl on these concentrated solutions. Hence, even if alumina particles represent only a small fraction of the total aerosol loading, they have the potential to affect, at mid-latitudes, the partitioning of chlorine between active and inactive forms.

In summary, the ozone depletion potential of SRMs could be significantly larger than that estimated on the basis of chlorine emissions alone, if the catalytic efficiency for chlorine activation by alumina particles is taken into account.

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Table 1. Average results from experiments¹.

	Glass Tube	Glass Beads	α -Alumina
$\langle k_{\text{obs}} \rangle$	$177 \pm 18 \text{ sec}^{-1}$	$153 \pm 10 \text{ sec}^{-1}$	$138 \pm 11 \text{ sec}^{-1}$
$\langle \gamma_{\text{measured}} \rangle$	$.022 \pm .005$	$.017 \pm .002$	$.014 \pm .002$

$$\gamma_{\alpha\text{-alumina}} = \gamma_{\text{glass}} \cdot \frac{\gamma_{\alpha\text{-alumina, measured.}}}{\gamma_{\text{glass beads, measured.}}} = .019 \pm .005$$

¹ Results are an average of 10 points each.

ClONO₂ + HCl on Glass Tube at -60 °C

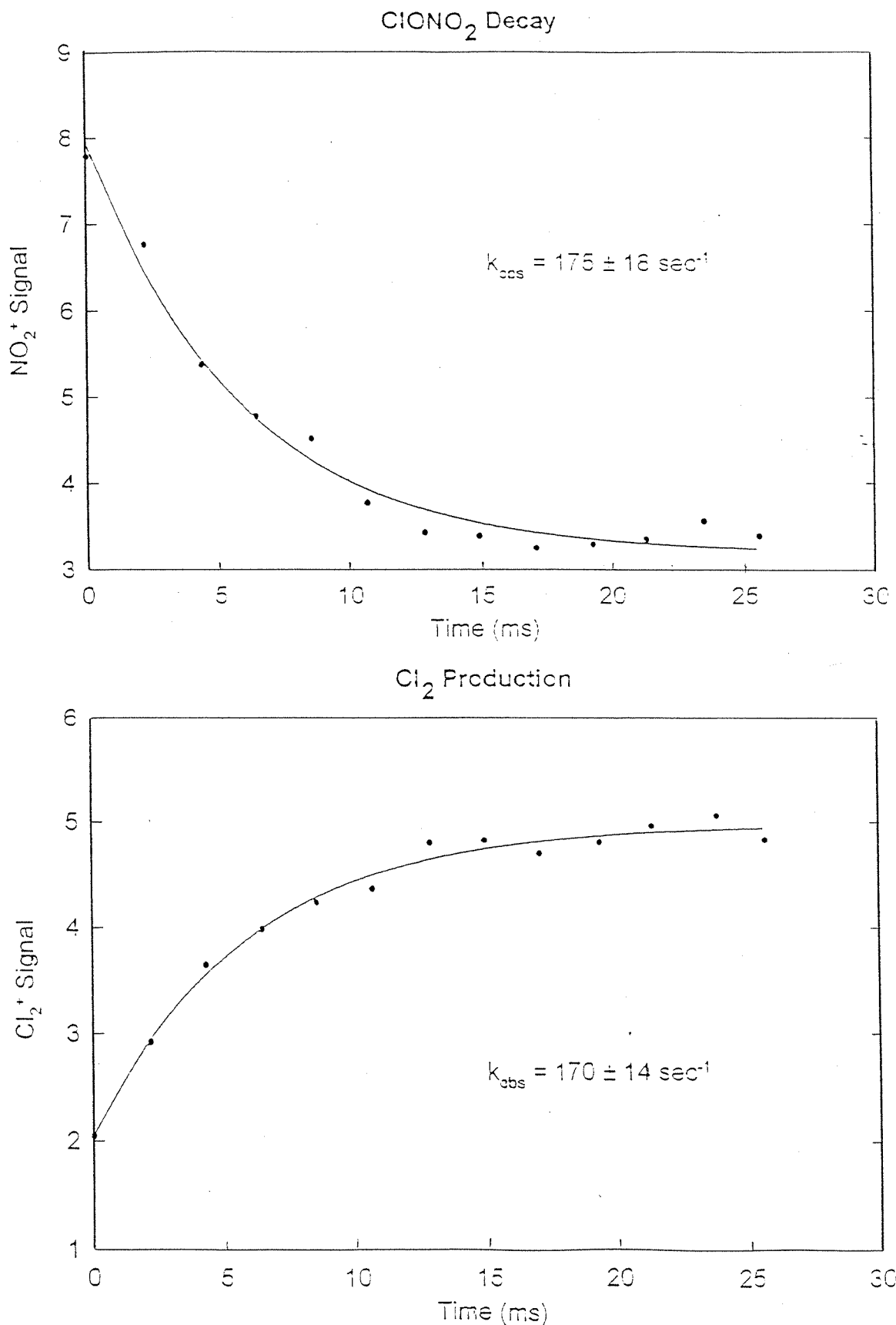


Figure 1. [ClONO₂] = 7.54x10⁻⁷ Torr, [HCl] = 7.46x10⁻⁶ Torr, [H₂O] = 4.81x10⁻⁴ Torr

ClONO₂ + HCl on Glass Beads at -60 °C

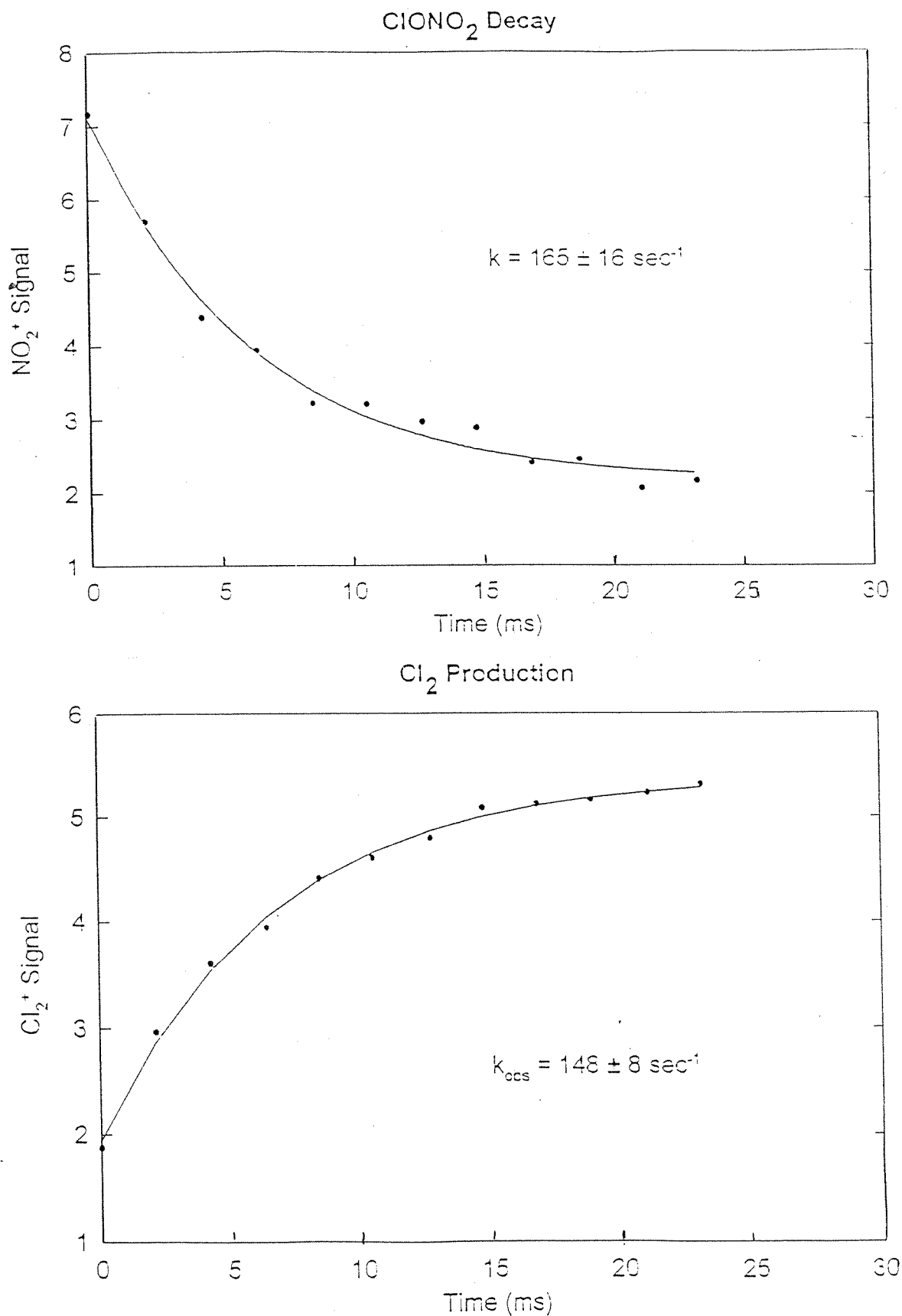


Figure 2. [ClONO₂] = 7.81×10⁻⁷ Torr, [HCl] = 7.71×10⁻⁸ Torr, [H₂O] = 4.57×10⁻⁴ Torr

$\text{ClONO}_2 + \text{HCl}$ on α -Alumina at -60°C

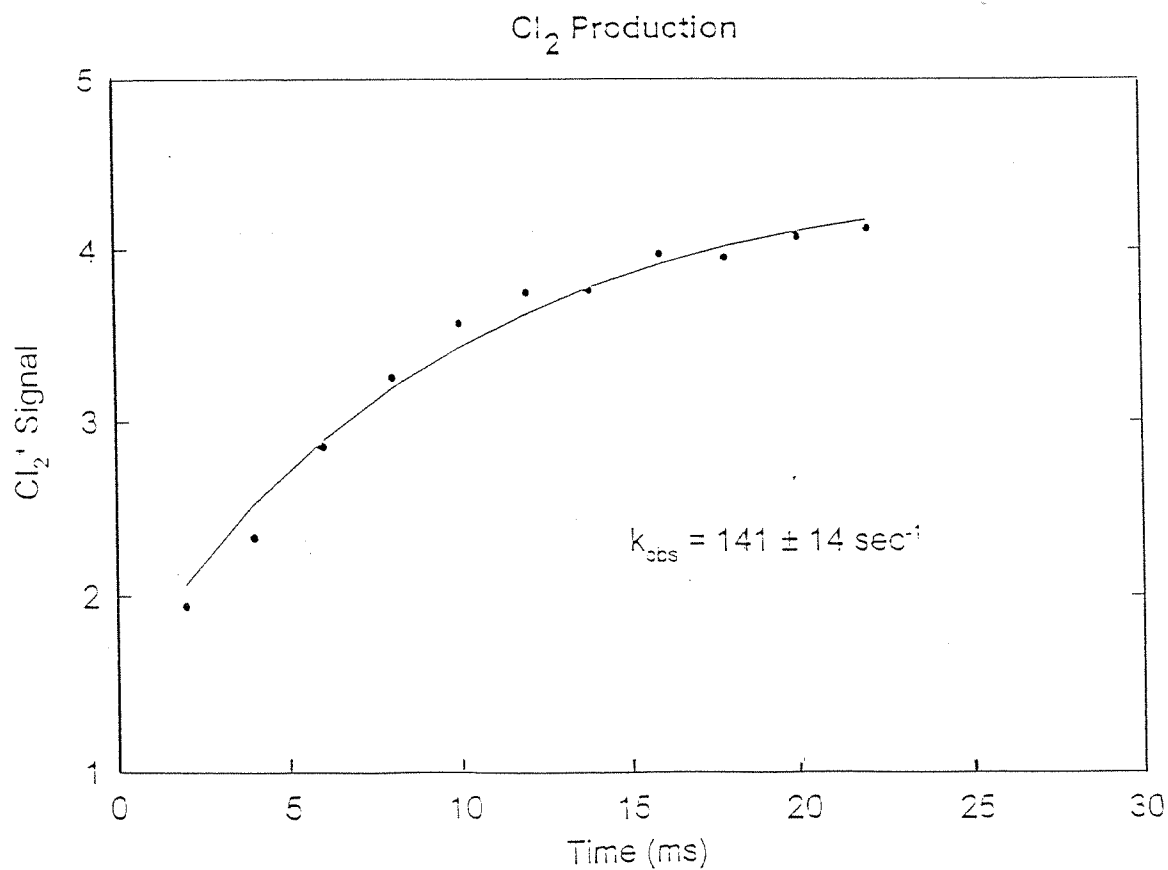
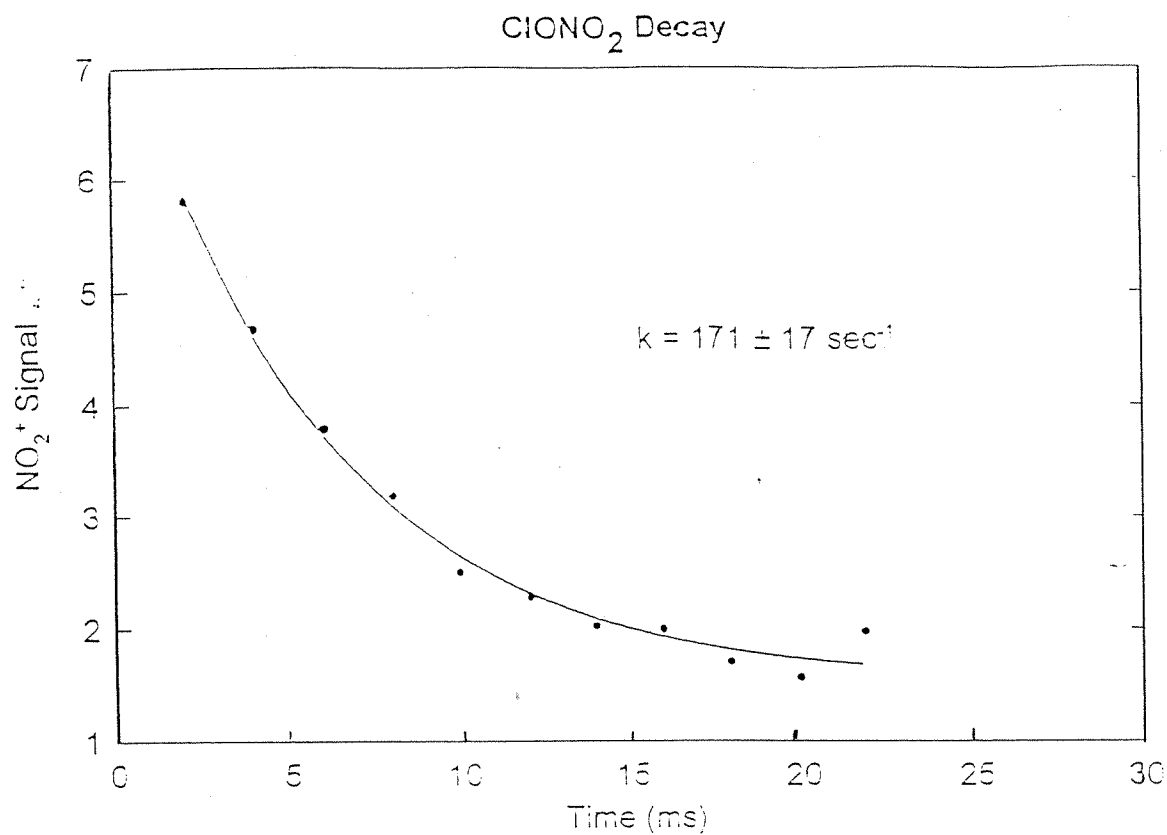


Figure 3. $[\text{ClONO}_2] = 7.56 \times 10^{-7} \text{ Torr}$, $[\text{HCl}] = 8.33 \times 10^{-6} \text{ Torr}$, $[\text{H}_2\text{O}] = 4.41 \times 10^{-4} \text{ Torr}$